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Copper emission factors from intensive shrimp aquaculture

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Emission factors, i.e., the amount of a given pollutant emitted per unit of production goods or production area, are strong tools for estimating pollutant loads to the environment from a variety of anthropogenic sources, since they can derive a difficult measurable variable (pollutant load) from an easily assessed parameter (e.g., area, amount of goods produced, inhabitants) and have been successfully used at the global (e.g., Nriagu and Pacyna, 1988); regional (e.g., Hutton and Symon, 1986) and local level (e.g., Molisani et al., 2004; Lacerda et al., 2006), to estimate pollutant emissions from natural and anthropogenic sources to the environment. Emission factors are also presently used in most countries' environmental agencies to create and update pollutant inventories statistics (e.g., EEA, 1999; EPA, 2002; Molisani et al., 2004).

The fast growth of intensive shrimp farming worldwide and its dependence on large inputs of artificial feed, fertilizers and of other chemical addictives such as acidity correctors and algaecides have triggered many studies to investigate shrimp farm's role as nutrient sources to coastal environments which allowed the calculation of emission factors for major nutrients such as N and P (Páez-Ozuna et al., 2003; Burford et al., 2003).

Trace metals, however, are not obvious pollutants present in shrimp farm effluents. However, some trace metals are present as natural components in aquafeeds, as impurities in fertilizers or as active principles of pesticides (Boyd and Massaut, 1999; Tacon and Forster, 2003). But since shrimp farming is generally developed in areas without significant sources of trace metals, their emissions can be relatively important for these regions. Among the trace metals eventually present in shrimp farm effluents, Cu is of high significance not only due to its ubiquitous presence in aquafeeds and other chemicals and to its toxicity to phytoplankton and the shrimps proper (Bainy, 2000; Chen and Lin, 2001; Lee and Shiau, 2002).

Shrimp farming in NE Brazil has increased exponentially during the past 10 years from an annual production of about 7000 tons, produced in less that 1000 ha of pond area in 1998 to over 90000 tons produced in about 15000 ha of pond area in 2003 (Madrid, 2004). This resulted in an increase in nutrient emissions to estuaries in many areas, which formerly had no significant pollution sources. A previous survey of trace metal content in shrimp and aquafeeds performed in some major farms in this area showed relatively high concentrations of Cu and suggested deleterious effects of this trace metal on shrimp productivity (Lacerda et al., 2004). In the present study we present the first estimate of Cu emission factor from intensive shrimp farming based on experimental data from a typical farm in Northeastern Brazil. The high similarity of emission factors for N and P from these farms and their technological processes with those generated from farms in Mexico and Australia (Páez-Ozuna et al., 2003; Burford et al., 2003; Jackson et al., 2003; Lacerda et al., 2006), suggests that the proposed emission factor for Cu may be applied for the shrimp farming industry worldwide.

Copper emission factor was generated by analyzing Cu concentrations in aquafeeds and other chemical addictives, in shrimp biomass and in inflow and outflow water and suspended particles and in pond bottom sediments of the largest shrimp farm of Ceará State NE Brazil, located at the Jaguaribe River estuary, latitude 4°23′ S and longitude 37°36′ W. Table 1 shows the major production parameters of the farm used in the calculation of the emission factor. These parameters are typical of intensive shrimp farming in Brazil and similar to those verified in shrimp farming worldwide.

Samples for Cu determination were collected during one production cycle using clean procedures. Water samples in the inflow canal, inside two ponds and in the outflow canal

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Table 1

Management characteristics of the studied shrimp farm at the Jaguaribe River estuary, NE Brazil

Parameter	Dimension
Pond size	3.2 ha
Pond depth	1.5 m
Water management	First 30 days without renewal. 5% daily volume renewal onwards
Growth cycles per year	2.3
Approximate growth period	135 days
Shrimp production	4540 kg ha^{-1} cycle^{-1}
Aquafeeds consumption	7940 kg ha^{-1} cycle^{-1}
Lime application	2370 kg ha^{-1} cycle^{-1}
Fertilizer application	46 kg ha^{-1} cycle^{-1}

were collected using pre-cleaned 1.5 L PET bottles. Samples were filtered non-longer than 3 h from collecting through acid-cleaned cellulose acetate filter with 0.45 μ of pore diameter for the collection of total suspended solids. Bottom sediments were sampled by hand directly in pre-cleaned plastic bags in different sites of the two ponds. During the growth cycle shrimps were sampled monthly and separated in muscle tissue and exoskeleton for analysis. Sediments and shrimps were kept frozen till analysis. Samples of 15 brands of aquafeeds, fertilizers and other chemical addictives used in the Jaguaribe Estuary shrimp farms were also analyzed. All solid samples were oven-dried to constant weight and ashed (450 °C/24 h) to remove the organic matter.

Filtered water samples were acidified and UV-treated to release Cu from strong organic complexes. Cu concentrations were determined by graphite furnace atomic absorption spectrophotometry. Ashes from solid samples were digested in 20 mL of 50% *aqua regia* solution for 2 h in Teflon crucibles at 80 °C. Simultaneously standard reference material NIST 2976 (mollusk tissue) and NIST 1646a (estuarine sediments) were treated similarly. The acid extracts were analyzed by conventional flame atomic absorption spectrophotometry in a Shimadzu AA-6200 spectrophotometer. Table 2 shows the comparison between certified and measured concentrations showing good recuperation of the certified concentrations, 92% for mollusk tissue and 88% for estuarine sediments.

Different aquafeed brands used in the studied farm showed average Cu concentrations ranging from 13.1 to 79.0 μg g^{-1} d.w. Concentrations in fertilizers varied from 0.7 to 2.0 μg g^{-1} d.w., whereas in other chemicals (lime and chloride) Cu concentrations varied from 1.9 to 3.3 μg g^{-1} d.w. (Table 3). Aquafeeds are by far the largest

Table 2

Comparison between Cu concentrations (μg g^{-1} d.w.), mean and standard deviation, in certified reference samples (National Institute of Standards & Technology – NIST) with those analyzed in the present study

Standard	n	Certified value	Measured value
NIST 1646a Estuarine Sediment	6	10.01 ± 0,34	8.8 ± 0.1
NIST 2976 Mollusk tissue	6	4.02 ± 0,33	3.7 ± 0.6

Table 3

Copper concentrations (μg g^{-1} d.w., mean and standard deviation) in different brands of aquafeed[*], fertilizers and other chemicals frequently in use by the studied farm

Substance	n	Cu
Dolomite lime	4	3.3 ± 0.2
Dolomite lime	4	1.9 ± 0.1
Granulated Chloride	3	3.3 ± 0.3
NutriLake (Fertilizer)	5	0.7 ± 0.3
Super phosphate	5	2.0 ± 0.2
Aquafeed 01	5	34.3 ± 0.8
Aquafeed 02	5	13.1 ± 1.0
Aquafeed 03	5	47.8 ± 0.1
Aquafeed 04	5	79.0 ± 5.0
Aquafeed 05	5	51.9 ± 0.1
Aquafeed 06	5	51.9 ± 1.3
Aquafeed 07	5	44.6 ± 0.1
Aquafeed 08	5	50.5 ± 2.4
Aquafeed 09	5	51.0 ± 13.5
Aquafeed 10	5	41.0 ± 15.1

[*]Since we are not a certified official laboratory we are not allowed to give the names of brands analyzed.

contributor of Cu to shrimp ponds due to the higher Cu concentrations and the larger amount used.

Suspended particulate matter (TSS) was higher (80–164 mg L^{-1}) in input waters than in pond waters (62 mg L^{-1}) and also higher than in renewal waters (87 mg L^{-1}). Extremely high TSS content was determined in bottom draining waters (1675 mg L^{-1}), a 19-times increase relative to surface waters. This suggests that at the end of the cycle when the pond is emptied, water currents moving into the central draining canal may be strong enough to erode and transport at least the surface nefloid layer of bottom sediments. Figueiredo et al. (2005) analyzing TSS balance in another farm at the Jaguaribe River using a similar cultivation processes found a 17-times TSS increase in bottom waters relative to surface waters. These authors monitored the emptying process and found that TSS-enriched waters represents about 20% of the total pond volume.

Copper concentrations in all analyzed samples are presented in Table 4. Average dissolved Cu concentrations were similar between input (7.2 μg L^{-1}) and output water (6.9–7.2 μg L^{-1}), resulting in no statistically significant net export of dissolved Cu to adjacent mangrove waters. Particulate Cu concentrations were higher in input waters (3.7–9.5 μg L^{-1}) than in pond (2.6–3.3 μg L^{-1}) and renewal output water (3.0–3.3 μg L^{-1}). However, the high TSS content of draining output water resulted in much higher particulate Cu concentrations (114 μg L^{-1}) resulting in a net export of particulate Cu of about 168 g ha^{-1} cycle^{-1}. This behavior is similarly to N and P behavior reported in other studies (Figueiredo et al., 2005), and represents the major form of Cu export from the ponds. Nutrients, in particular N and P export from shrimp farming is (~60% and >98% for N and P, respectively) constituted by particulate forms mostly released during the end of the draining process